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Deuterium NMR has been used to probe the molecular dynamics and structure of the surfactant sodium 4-(1'-heptylnonyl)benzenesulfonate (SHBS) adsorbed from water solution onto alumina. In order to investigate the dynamics of the headgroup, the phenyl ring of the surfactant was specifically deuterated. Two different surface coverages were studied in the temperature range of -30 °C to 80 °C. At the adsorption plateau, evidence for the presence of two distinct surfactant domains of approximately equal intensities, on the alumina surface, was found. One domain, the inner layer next to the solid surface, gave rise to a quadrupole splitting in the ^2H NMR spectrum similar to that found for the surfactant in lamellar liquid crystals; whereas the second domain, the outer layer, gave rise to a broad unsplit resonance indicating a more isotropic environment. The chemical exchange between the two domains was found to be slow on the NMR timescale. At a lower coverage, a broad unsplit resonance appeared in the NMR spectrum showing that the molecular motions are not sufficiently anisotropic to cause any observable quadrupole splittings. With increasing temperature, resonances for both samples were narrowed, and the quadrupole splitting was reduced, reflecting more rapid reorientations of the surfactant molecules.

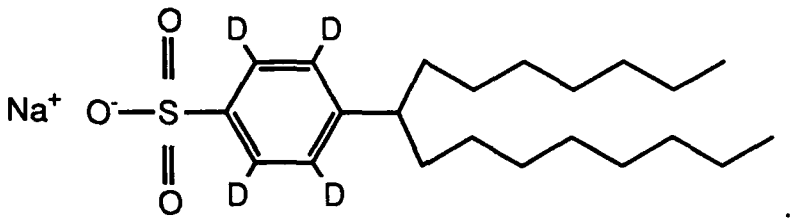
INTRODUCTION

The adsorption of surfactants from solution onto solid surfaces is of broad interest in different fields, such as flotation, detergency, oil recovery, and fabric softening (1). The adsorption of ionic and nonionic surfactants, and even mixtures of surfactants, on either metal oxides or polymers, have been reported. Most of the prior studies studies have focused mainly on establishing adsorption isotherms (2-5). The adsorption isotherms found were typically *S*-shaped with a plateau reached around the critical micelle concentration, *cmc*, of the surfactant. The nature of the adsorbed surfactants in terms of their structure and mobility is far from established in spite of their importance.

In many cases, the plateau of the adsorption isotherm is believed to be consistent with the formation of a double layer of surfactant at the water/solid interface (4-10). This double layer, or bilayer, is believed to consist of an inner layer with the surfactant headgroups near the solid surface, and an outer layer with the headgroups away from the surface (8). Neutron reflection studies of hexadecyltrimethylammonium bromide adsorbed on amorphous silica were consistent with the formation of a surfactant double layer even below the *cmc* (11). The reversal of the sign of the ζ-potential of alumina particles as sodium undecenoate is adsorbed to the plateau value (12-13) also supports the double layer model. Sodium dodecanoate adsorbed on alumina has also been reported to form a double layer (14). The structure of the surfactant below the adsorption maximum is less clear. Alkylbenzenesulfonate bilayers on alumina were reported to be formed in patchwise discontinuous fashion and have been dubbed *admicelles* for which an adsorption model has been developed (9-10). Alternatively, other workers have reported the possibility of monolayer formation as in the case when sodium dodecylsulfate is adsorbed on alumina (15-17). Compact monolayers have also been proposed for surface adsorbed micelles and dubbed *hemimicelles*. (18-19)

In this paper, we present ^2H NMR results for the double-tailed surfactant sodium 4-(1'-heptylnonyl)benzenesulfonate, specifically ^2H-labeled on the phenyl ring (SHBS-d_4), adsorbed on

γ-alumina as a function of coverage and temperature. The structure of the surfactant is shown below:



It has previously been shown that ^2H NMR spectroscopy is applicable for studying the molecular dynamics in the adsorbed layer (20), and in this work, we show how a straightforward analysis of the deuterium lineshape can be utilized for describing the dynamics and structure on the molecular level. The ^2H NMR spectra are sensitive to whether a monolayer or bilayer is formed on the surface as the surfactant is adsorbed. The results are presented in comparison with those obtained from lamellar liquid crystalline systems, as there is significant similarity in both states.

The adsorption of surfactants similar to SHBS on solid surfaces has previously been studied. The plateau adsorption of sodium octylbenzenesulfonate on α-alumina has recently been shown to reach a maximum at pH 5 (21). An adsorption of about 7 $\mu mol/m^2$ was reported for the plateau value. Similar plateau values were obtained in a study of double-tailed alkylbenzenesulfonates adsorbed on γ-alumina (9). Maximum adsorption was obtained at pH 4 and surfactant concentration close to the *cmc*. The surface area occupied per surfactant molecule at the plateau was found to be 40-50 $Å^2$, assuming a bilayer was formed. This correlated well with air-water interfacial densities for those surfactants. In general, the adsorption is not very dependent on the type of alumina, but the changes in the surface charge density with pH create a strong pH dependence. The maximum adsorption also increased slightly with hydrocarbon chain length. The alkylbenzenesulfonates studied (9) resembled SHBS, but the lengths of the hydrocarbon chains were shorter and exhibited micelle formation.

SHBS is one of a series of linear alkylbenzenesulfonates that have been synthesized and characterized with respect to the interfacial tension between water solutions of the surfactants and

alkanes, alkylbenzenes, or alkylcyclohexanes (19). SHBS has also been subject to a number of studies focusing on the phase behavior of the surfactant in water and the molecular dynamics of the surfactant in those phases. It has been shown that SHBS forms weak aggregates below its solubility limit. However, no cmc in water has been found. Instead, the surfactant forms lamellar liquid crystals. The transformation to the liquid crystalline phase occurs over a broad biphasic region consisting of the liquid crystalline phase in equilibrium with a dilute isotropic SHBS solution (23-25). In aqueous dispersions of the liquid crystals, vesicles or liposome-type structures can be formed by sonication or mechanical agitation (26-30). Those structures have been found to be relatively stable at room temperature. In multilamellar liposomes, the original form can be recovered by heating of the dispersions (27). The surfactant also has good biological and chemical stability, making it suitable for long term studies and at elevated temperatures.

MATERIALS AND METHODS

Materials

The synthesis of the surfactant SHBS has been described elsewhere (22). The SHBS-d_4 was specifically labeled in the phenyl ring by starting with benzene-d_6 in the preparation of the surfactant (31). The surfactant was dried in a vacuum oven for 24 hours at 60 °C before use. The adsorbent used was γ-alumina obtained from Johnson Matthey (Ward Hill, MA). According to the manufacturer's specification, it was 99.99 % pure and the average particle size was 10 nm. The N_2-based BET surface area was determined to 103 m^2/g. The alumina was dried in a vacuum oven for 24 hours at 100 °C before use. Deuterium depleted water, obtained from CIL (Woburn, MA), was used throughout the adsorption experiments.

Sample Preparation

Two samples were prepared with a similar procedure. Dried alumina (1-2 g) was weighed into a screw capped vial to which a solution of 0.10 M NaCl and 0.10 M HCl was added to make up a suspension with a solids content of 10 % by weight. The pH of the suspension was about 4. Approximately 0.4 g (1 mmole) of the SHBS-d_4 was placed in the vial. The mixture was stirred with a magnetic stirrer for several days at room temperature. Occasionally the sample was sonicated for typically 2 hours, and then stirred again. A part of the suspension was then transferred into a centrifugation tube and was centrifuged for 15-20 minutes at 3000 rpm. The excess supernatant, approximately 70 % of the total amount of solution, was clear after the centrifugation. It was removed and the residual thick mixture was transferred into a 5 mm NMR tube which was then sealed.

Several adsorption isotherms for the adsorption of alkylbenzenesulfonates on alumina are known. At pH = 4, the maximum adsorption varies between Γ = 7 to 9 $\mu mole/m^2$, depending on the alkyl chain length (9,21). In order to obtain different amounts of adsorbate on the surface for two samples, the amount of alumina was varied. In sample II, approximately 1 g of the alumina

was used, corresponding to a total surface area accessible for adsorption of 103 m^2. The SHBS-d_4 concentration in the supernatant of this sample was determined with a UV spectrophotometer (Shimadzu, UV-110-02) to be 1.1 mM, corresponding to an adsorption of $\Gamma = 9$ μmole/m^2. Thus, maximum adsorption was obtained, and the surfactant concentration in the supernatant solution was close to the solubility limit. In sample **I**, twice the amount of alumina (and HCl/NaCl solution) was added, and the adsorption was well below the plateau value according to the adsorption isotherms. The adsorption in sample **I** was within a region which can be considered as the intermediate adsorption region, where the surfactant concentration normally is under the *cmc* (9). In both samples, over 80 % of the surfactant was adsorbed, based on available adsorption isotherms (9,21).

A third NMR sample was made by mixing SHBS-d_4 with water to a concentration of 2 % by weight. The solution was treated similarly to the samples for adsorption, including stirring, sonication and centrifugation. The surfactant concentration puts it in the biphasic region, however, the treatment of the dispersion breaks the liquid crystalline structure and other aggregates, *i. e.* vesicles, are produced (30). The solution was translucent and blueish, indicating presence of small particles. Those aggregates did not form a sediment during the centrifugation.

Deuterium NMR

NMR spectroscopy has been widely used for studying the molecular dynamics of surfactant systems (32). Deuterium, with spin quantum number $I = 1$, has been particularly useful for these systems. A deuterium nucleus possesses an electric quadrupole moment, and its interaction with the electric field gradient, EFG, at the nucleus perturbs the nuclear Zeeman energy levels (33). The magnitude of this perturbation is determined by the orientation of the external magnetic field with respect to the principal axes of the EFG tensor, which is often axially symmetric for C-^{2}H bonds. The resulting quadrupole splitting, Δ, is defined as the separation between the two allowed transitions for the deuterium nuclei. In liquid systems, the quadrupole interaction is averaged out, but for static systems powder or Pake patterns are obtained. Molecular motions that are on the

order of, or fast, compared to the quadrupole coupling constant will affect the lineshape and reduce the splitting from its rigid value. The observed splitting for a partially averaged spin system, having an axially symmetric EFG tensor, can generally be expressed as

$$\Delta = \frac{3}{2}\chi\left|\left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle\right| \qquad [1]$$

where χ is the quadrupole coupling constant, the brackets ($\langle\ \rangle$) denote the time average, and θ is the time dependent angle between the C-^{2}H bond and the external magnetic field.

For ordered systems, such as lamellar liquid crystals or bilayers on solid surfaces, it is instructive to view the system and its motion from a molecular point of view. The alkylbenzene-sulfonate used in this study was deuterated in the 2-, 3-, 5-, and 6-positions of the phenyl ring. Therefore it is appropriate to introduce three frames of reference. The relevant axes of those frames are the symmetric 1,4-axis of the phenyl ring (**M**), the director or normal to the bilayer (**N**), and the direction of the external magnetic field ($\mathbf{B_0}$). The orientational relationship between those three axes is shown in Figure 1. Equation 1 can be rewritten in terms of α, β, and γ, as defined in Figure 1. For a single crystallite, in which the ring undergoes a fast rotation about **M**, and the director is stationary with respect to $\mathbf{B_0}$, the observed splitting is given by

$$\Delta = \frac{3}{2}\chi\left|\frac{3\cos^2\alpha - 1}{2}\right|\left|\frac{3\cos^2\gamma - 1}{2}\right|\left|\left\langle \frac{3\cos^2\beta - 1}{2} \right\rangle\right| \qquad [2]$$

The time average of $\langle(3\cos^2\beta - 1)/2\rangle$ is the local order parameter and often noted S (32). The spectrum observed for a powder sample is a Pake pattern, provided S is non-zero, due to the distribution of directors, **N**, of the individual crystallites. The splittings will be reduced from their static values because of the motion. The separation of the most prominent components or "horns" of the spectrum is obtained with $\alpha = 90°$ and $\gamma = 60°$ in Equation 2 or

$$\Delta(90) = \frac{3}{32}\chi|S| \qquad [3]$$

In addition to the reduction in the quadrupole splitting due the the fast rotation about the phenyl-ring symmetry axis, further reduction may result from the motion of the ring relative to the director. These fluctionations are probably symmetric about the director so that $<\beta> = 0°$. This will have the effect of reducing the value of *S*, but not eliminating it because β is not isotropically averaged over the NMR timescale.

Deuterium spectra were recorded on a Varian VXR-200 NMR spectrometer equipped with a wide-line probe. Spectra were obtained at 30.7 MHz using a quadrupole echo sequence

$$(\pi/2)_x\text{-}\tau\text{-}(\pi/2)_y\text{-}\tau\text{-acq.}$$

The $\pi/2$ pulse was adjusted to 2 μs and the delay between the pulses was kept at 40 μs. The recorded spectra were obtained with a spectral width of 100 kHz, 8192 points, 20 000 transients and a line broadening of 100 Hz. When changing the temperature in the probe, less than 10 minutes were required to establish thermal equilibrium (31). Spectra were also recorded at 25 °C before, just after, and several weeks after the multi-temperature experiments, and no significant changes in the spectra were observed.

RESULTS

The ^2H NMR spectra of SHBS-d_4 from sample I, sample II, the 2 % water solution, and the liquid crystalline state at 25 °C are shown in Figure 2. The spectrum of the liquid crystalline material is similar to that previously reported (31), and is shown for comparison. The spectrum of SHBS-d_4 in solution consists of a narrow resonance, showing that no significant amount of large liquid crystals were present in the sample. Even though the concentration of surfactant was such that it was close to the biphasic region, stirring and sonication transformed any liquid crystals present into other non-equilibrium, but kinetically stable aggregates, *i.e.* small vesicles (34), which do not show quadrupole splittings in the NMR spectrum. The spectrum of sample **II**, in which the adsorption plateau is reached, clearly consists of two components. A powder pattern is superimposed on a relatively narrow central resonance. The spectrum of sample **I** shows only a single resonance. However, this resonance is significantly broader than the central resonance in the spectrum of sample **II**.

Shown in Figure 3 are the spectra of sample **II**, obtained from -30 to 80 °C. At -30 °C, a narrow weak resonance is superimposed on a broad resonance. No quadrupole splitting is observed. This spectrum was also obtained with greater spectral width, 2 MHz, but no other features were found. At -20 °C, the broad component is narrowed, and a definite appearance of a powder pattern is present. From -10 up to 80 °C, all the spectra have essentially the same features. The quadrupole splittings can clearly be seen, and there is also a narrower nearly isotropic resonance. This resonance narrows as the temperature increases. The ratio of the intensities, *i.e.* the integrals, of the two resonances remains constant at approximately 1 above 0 °C, with a slightly greater integral for the powder pattern. The central resonance height increases with temperature because it narrows. The spectra at 65 °C and 80 °C have been truncated to more clearly show the splitting in the powder pattern. The spectrum recorded at 25 °C has also been enlarged in Figure 3 to show the broader features. The lineshape of the powder pattern remains constant, but the observed quadrupole splitting for the 90° orientation, $\Delta(90)$, is slightly reduced at higher

temperatures. At -10 °C Δ(90) is 12 kHz, and is reduced to 10.3 kHz at 80 °C.

Although not shown here, spectra were also recorded at -40 °C and -65 °C. At those temperatures, all motions on our experimental timescale are frozen out, and a standard Pake pattern corresponding to a rigid system is observed. A Δ(90) of 128 kHz was found, which agrees well with previously determined values for this surfactant (31). This implies a quadrupole coupling constant of about 171 kHz.

In Figure 4 the spectra from sample **I** are shown at -20, 0, 25, and 65 °C. These spectra consist of a single resonance, which is very broad at -20 °C, but is considerably narrowed as the temperature is increased. No quadrupole splittings are resolved in the spectra, not even at the lower temperatures. The spectra recorded at low temperatures (-20 °C and -30 °C) of samples **I** and **II**, all show a reduced intensity in comparison to spectra obtained with the same number of transients at higher temperatures. A similar intensity reduction is found in the spectra of SHBS in lamellar liquid crystals in this region (31). This type of reduction is probably due to motions with frequencies on the order of the quadrupole echo time.

DISCUSSION

NMR studies of SHBS liquid crystals have concentrated on the behavior of the water in the bilayers. Multi-temperature ^{13}C NMR studies of SHBS have revealed a motional gradient within the hydrocarbon tail, with the more restricted motions toward the head group (35). In a recent ^{2}H NMR study of the liquid crystalline phase of SHBS-d_4, the molecular motions of the head group were identified (31). Experimental ^{2}H NMR spectra were interpreted by comparing them with simulated spectra. Different molecular motion models were applicable in different temperature regions. At low temperatures (< -20 °C), 2-fold ring flips and rotations of the molecule in an anisotropic medium were consistent with the lineshapes. At higher temperatures, (> -20 °C), an anisotropic viscosity model was required to get good agreement with experimental spectra.

It is clear from Figure 2, that SHBS-d_4 molecules adsorbed on alumina give rise to broad resonances, which are broader than those found in solution or aggregates like vesicles. At low coverage (sample **I**), from the available adsorption isotherms (9,21), we estimate that at equilibrium, over 90 % of the surfactant molecules in the sample are adsorbed on the surface. After centrifugation, the sediment contained approximately 30 % of the initial amount of solution, and the solids content was increased from the initial 10 % to about 25 % by weight. Consequently, the sediment, which was transferred to the NMR tube, contained a relatively large amount of the surfactant and the spectrum of sample **I** (Figure 2A) is dominated by the adsorbed molecules. As the resonance of dissolved surfactant molecules is very sharp relative to that in Figure 2A, its superposition on the broad component would clearly be observed even though less than 10 % of the surfactant molecules are dissolved. The fact that no superposition is observed in the spectrum implies that the exchange of molecules between solution and surface is relatively fast. This is consistent with previous studies of surfactants adsorbed on solid surfaces (20). Since the spectrum in Figure 2A consists of only one single resonance without quadrupole splitting, the adsorbed molecules experience a more isotropic environment, compared to that in the liquid crystal. There may still be some residual anisotropy in the system, but any residual quadrupole

splitting is less than the linewidth of the resonance.

Line shapes similar to those observed for sample I have been reported for deuterated alkyl-modified silicas (36,37) in the presence of solvent. These lineshapes have been explained by a combination of the presence of slow motions and the absence of unique axes of reorientation (as opposed to that in solution). However, the linewidths observed are indicative of a fair amount of mobility They occur for labelled species towards the middle or ends of solvated attached species with alkyl lengths around 10 to 18 carbons long. Short terminally attached chains, such as aminopropylsilane and aminobutylsilane show much more restricted motion (38) as do longer chains labelled closer to the point of attachment. (36) In contrast to the chemically attached alkyl chains, SHBS molecules were not rigidly bound to the surface and motions, such as lateral diffusion along the surface, were possible. In addition, chemical exchange between surface and solution SHBS also contributes significantly to the averaging of any quadrupolar interactions that may be present.

The two discrete parts of the lineshape in Figure 2B imply that at least two different domains for SHBS molecules exist, and they are in slow exchange with each other. A comparison of this spectrum with that from 2 % SHBS-d_4 in water (Figure 2C), suggests that both the powder pattern and the broad central resonance originate from molecules spending at least some of the time adsorbed on the surface. Hence, there are two different environments for the molecules on the surface at this coverage. The integrals of the central resonance and the powder pattern are nearly equal, with the domain giving rise to the splitting has a slightly larger fraction of the total number of adsorbed molecules. The powder pattern resembles the spectrum of liquid crystals (31), while the central peak again reflects more isotropic, but not solution-like molecular motions. The mobility of this domain must be somewhere in between that of the molecules in a liquid crystal or in solution, even if they are in moderate sized aggregates such as vesicles. Overall rotation of the vesicular aggregates is not a possibility for the surface adsorbed species on the NMR timescale.

A picture consistent with these observations is that an adsorbed double layer exists and is comprised of a first (inner) layer, in contact with the surface, and a second (outer) layer with the

head groups pointed towards the solution. These two layers are in slow exchange and give rise to the two component spectrum observed in Figure 2B. The small differences between the integrals for each may be a result of a less dense packing in the outer layer. The inner, motionally restricted domain experiences a mobility which is very similar to that in the liquid crystal. The outer domain may have some similarities to the liquid crystal, but the lower packing density, and exchange with surfactant in solution, should significantly narrow the resonance. Fast chemical exchange between these two environments would lead to a resonance whose characteristics would be the mole fraction weighted average of the two.

The local order parameter, |S|, has been calculated from the observed splitting, $\Delta(90)$, and is displayed in Table I. The quadrupole splittings and the corresponding order parameters from the inner layer become smaller as the temperature increases, reflecting an increased local disorder in this layer. This behavior is similar to that found for SHBS-d_4 in liquid crystals, however, the order parameter for the inner adsorbed layer is measurably smaller. For example, at room temperature, the quadrupole splitting for the inner layer is 10.8 kHz and |S| = 0.67, while for the liquid crystal the splitting is 13.5 kHz and |S| = 0.84. Similar comparisons can be made across the entire temperature range (31). This implies that although the inner layer is relatively closely packed, each headgroup experiences greater motional freedom than in the liquid crystalline state.

The area per headgroup can be estimated from the adsorption isotherm. For alkylbenzenesulfonates, the average headgroup area on surfaces ranges from 40 to 50 $Å^2$, based on a bilayer structure (9,21). Our data for SHBS suggest about 37 $Å^2$ per headgroup which is smaller, but similar to the results of Scamehorn *et al.* (9). Those data should be compared with the area per headgroup in the liquid crystals. At this time no such data is available for double-tailed alkylbenzenesulfonates, which disables direct comparison. However, the area occupied by a single alkyl chain in the liquid crystalline state is 33 $Å^2$ and the area per group in a compact monolayer of sulfonates is 27 $Å^2$ (21). Clearly the situation for single and double-tailed surfactants is different. The only comparative study for a single-tailed surfactant did not show any evidence of liquid-

crystal behavior for the surface bound surfactant (20). The decreased area per headgroup is consistent with lower mobility and liquid-crystalline behavior for SHBS at the interface compared the behavior of single-tailed surfactants.

There are several models which describe the molecular motions in liquid crystals or membranes. One of those models include uniform diffusive wobbling in a cone (39). For this model, the order parameter is related to the half angle of the cone, θ_0, according to

$$|S| = \frac{1}{2}\cos\theta_0(1+\cos\theta_0) \qquad [4]$$

For comparison, we have applied this model to our data and calculated the half cone angles. These are shown in Table I, and are fairly wide in this system. At high temperatures, the cone half angle is around 40°, which is substantially wider than in the liquid crystalline system consistent with their greater spatial freedom.

Further comparison with the liquid crystalline system is appropriate. It has previously been shown that the splitting in the spectra of SHBS-d_4 in liquid crystals undergoes a transformation around -30 to -20 °C. This was consistent with the onset of fast rotational diffusion about the long axis of the molecule, *i.e.* the **M**-vector in Fig. 1. Ring flips begin at about -40 °C and at lower temperatures the ring is static. The flipping motion transforms into fast rotational diffusion, whose frequency and angular excursions also increase, with increasing temperature. At intermediate rotation frequencies, the intensity of the quadrupole-echo spectrum is significantly reduced. This corresponds to the temperature at which the quadrupole splitting disappears (-20 to -30 °C) for the inner layer surfactant.

Returning to the central resonance, its narrowness reflects the more rapid reorientations of the molecules in the outer layer, particularly as the temperature is increased. The same behavior is found for molecules adsorbed at lower coverages (Figure 4). In the latter case, the lineshape is narrowed considerably at higher temperatures. Another noteworthy feature of the spectra in Figure 3 is that the relative peak areas of the powder pattern and the narrow resonance are indifferent to

temperature changes. Hence, the distribution of molecules between the first and second layer is not influenced by the temperature and no exchange occurs between them on the NMR timescale.

Based on the information above, we are in a position to speculate on the adsorption behavior in the intermediate adsorption regime. *Surface micelles* (21), *hemimicelles* (18,19,40) and patchwise *admicelles* (9,10) have all been proposed for surfactant adsorption. Our data from the intermediate adsorption region show only one broad resonance which must be representative of at least two species in fast exchange. The separation into an inner and outer layer as observed for the high coverage does not occur. Thus patchwise aggregates or *admicelles* of any significant size which begin to resemble the full bilayers do not exist. Unfortunately, the present data can not distinguish between *hemimicelles* or *surface micelles* as either of these two structures may be mobile enough to allow exchange of the surface surfactant with surfactant either in solution or in an outer surface layer. It is not possible to determine the dynamics of the surface layer in detail at this point because of the exchange process. We hope to be able to address this question at a later date. In any case, with further adsorption leading to full bilayer formation, the exchange of surfactant in the inner layer is suppressed.

CONCLUSIONS

The present work shows that the headgroups of SHBS experience an relatively isotropic environment in solutions of vesicles, giving rise to a sharp resonance in the ^{2}H NMR spectrum. When adsorbed at maximum amount for a bilayer on alumina, two different domains are found. The domain next to the alumina surface (inner layer) is anisotropic giving rise to a quadrupole splitting in the ^{2}H NMR spectrum on the order of 10-12 kHz. Splittings found in lamellar liquid crystals of the same surfactant are similar, indicating that this domain resembles the liquid crystalline state. However, the splittings are slightly smaller than those in the liquid crystal indicative of a somewhat higher degree of motional freedom in the adsorbed layer. The other domain (outer layer), shows fewer motional restrictions which give rise to a broad, but unsplit resonance in the deuterium NMR spectrum. Chemical exchange between the two layers is slow on the NMR timescale.

At a lower coverage, the surfactant molecules next to the surface experience an environment which is averaged on the NMR timescale. The molecular motions at this coverage are not sufficiently anisotropic to cause observable quadrupole splittings in the spectrum. Either surface micelles or hemimicelles, but not admicelles, are consistent with the obtained lineshapes.

As the temperature is increased, the resonances in all the spectra are sharpened. The quadrupole splitting is reduced, corresponding to an increased motional freedom, or increased disorder, in both layers of the bilayer. The distribution of molecules between the first and second layer is not or only slightly dependent of the temperature.

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References

1. (a) Fuerstenau, D. W., and Herrera-Urbina, R. In "Cationic Surfactants: Physical Chemistry" (Rubingh, D. N., and Holland, P. M., Eds.). Marcel Dekker, New York, p 407 (1991).

   (b) Laughlin, R. G., In "Cationic Surfactants; Physical Chemistry" (Rubingh, D. N., and Holland, P. M., Eds.). Marcel Dekker, New York, p449 (1991).

   (c) Rubingh, D. N., In "Cationic Surfactants; Physical Chemistry" (Rubingh, D. N., and Holland, P. M., Eds.). Marcel Dekker, New York, p469 (1991).

2. Clunie, J. S., and Ingram, B. T. In "Adsorption from Solution at the Solid/Liquid Interface" (Parfitt, G. D., and Rochester, C. H., Eds.). Academic Press, San Diego, p 105 (1983).

3. Hough, D. B., and Rendall, H. M., In "Adsorption from Solution at the Solid/Liquid Interface" (Parfitt, G. D., and Rochester, C. H., Eds.). Academic Press, San Diego, p247 (1983).

4. Denoyel, R., Rouquerol, F., and Rouquerol, J., In "Adsorption from Solution" (Ottewill, R.H., Rochester, C.H., and Smith, A.L., Ed.). Academic Press, London, p225 (1983).

5. Ingram, B. T., and Ottewill, R. H., In "Cationic Surfactants; Physical Chemistry" (Rubingh, D. N., and Holland, P. M., Eds.). Marcel Dekker, New York, p87 (1991).

6. Gu, T., and Zhu, B.-Y., *Adv. Colloid Interface Sci.* **37**, 1 (1991).

7. Esumi, K., Nagahama, T., and Meguro, K., *Colloids Surf.* **149**, 57, (1991).

8. Pashley, R. M. and Israelachvili, J. N., *Colloids Surf.* **2**, 169 (1981).

9. Scamehorn, J. F., Schechter, R. S., and Wade, W. H., *J. Colloid Interface Sci.* **85**, 463 (1982).

10. Harwell, J.A., Hoskins, J.C., Schecter, R.S., and Wade, W.H., *Langmuir* **1**, 251 (1985).

11. Rennie, A. R., Lee, E. M., Simister, E. A., and Thomas, R. K., *Langmuir* **6**, 1031 (1990).

12. Esumi, K., Watanabe, N., and Meguro, K., *Langmuir* **5**, 1420 (1989).

13. Esumi, K., Watanabe, N., and Meguro, K., *Langmuir* **7**, 1775 (1991),

14. Ruths, M., Sjöblom, J., and Blokhus, A. M., *J. Colloid Interface Sci.* **145**, 108 (1991).

15. Sjöblom, J., Blokhus, A. M., and Höiland, H., *J. Colloid Interface Sci.* **136**, 584 (1990).

16. Sjöblom, J., Blokhus, A. M., Sun, W. M., and Friberg, S. E. *J. Colloid Interface Sci.* **140**, 481 (1990).

17. Blokhus, A. M., and Sjöblom, J., *J. Colloid Interface Sci.* **141**, 395 (1991).

18. Somasundaran, P., and Fuerstenau, D.W., *J. Phys. Chem.* **70**, 90 (1966).

19. Dick, S.G., Fuerstenau, D.W., and Healy, T.W., *J. Colloid Interface Sci.* **37**, 595 (1971).

20. Söderlind, E., and Stilbs, P. *J. Colloid Interface Sci.* **143**, 586 (1991).

21. Denoyel, R.; Rouquerol, J. *J. Colloid Interface Sci.* **143**, 555 (1991)

22. Doe, P. H.; El-Emary, M.; Wade, W. H.; Schechter, R. S., *J. Am. Oil Chem. Soc.* **54**, 570 (1977).

23. Miller, W. G.; Blum, F. D.; Davis, H. T.; Franses, E. I.; Kaler, E. W.; Kilpatrick, P.K.; Nietering, K. E.; Puig, J. E.; Scriven, L. E., In "Surfactants in Solution" (Mittel, K. L., Lindman, B., Eds.). Plenum Publishing, New York, Vol. 1, p175 (1984).

24. Franses, E. I.; Davis, H. T.; Miller, W. G.; Scriven, L. E. In "Chemistry of Oil Recovery" (Johansen, R. T., Berg, R. L., Eds.). American Chemical Society: Washington, DC, p35 (1979).

25. Kilpatrick, P. K.; Miller, W. G., *J. Phys. Chem.* **88**, 1649 (1984).

26. Kilpatrick, P. K.; Miller, W. G.; Talmon, Y. *J. Colloid Interface Sci.* **107**, 146 (1985).

27. Franses, E. I.; Talmon, Y.; Scriven, L. E.; Davis, H. T.; Miller, W. G., *J. Colloid Interface Sci.* **86**, 449 (1982).

28. Kaler, E. W.; Falls, A. H.; Davis, T. H.; Scriven, L. E.; Miller, W. G., *J. Colloid Interface Sci.* **90**, 424 (1982).

29. Madani, H.; Kaler, E. W., *Langmuir* **6**, 125 (1990).

30. Blum, F. D.; Franses, E. I.; Rose, K. D.; Bryant, R. G.; Miller, W. G., *Langmuir* **3**, 448 (1987).

31. Duke, J. R.; Funchess, R. B.; Blum, F. D., *Langmuir* **7**, 1909 (1991).

32. For a recent review see: Chachaty, C., *Prog. Nucl. Magn. Reson. Spectrosc.* **19**, 183 (1987).

33. Abragam, A. "The Principles of Nuclear Magnetism". Oxford University Press, Oxford (1961).

34. Johnson, N. W.; Kaler, E. W., *J. Colloid Interface Sci.* **116**, 444 (1987).

35. Blum, F. D.; Miller, W. G., *J. Phys. Chem.* **86**, 1729 (1982).

36. Gangoda, M.; Gilpin, R. K.; Figueirinhas, J., *J. Phys. Chem.* **93**, 4815 (1989).

37. Gangoda, M. E.; Gilpin, R. K., *Langmuir* **6**, 941 (1990).

38. Kang, H.-J. and Blum, F.D., *J. Phys. Chem.* **95**, 9391 (1991).

39. Vold, R. R.; Vold, R. L., *Adv. Magn. Optical Reson.* **16**, 85 (1990).

40. Chandar, P.; Somasundaran, P.; Turro, N. J., *J. Colloid Interface Sci.* **117**, 31 (1987).

Table I.

Observed quadrupole splittings, Δ(90), and corresponding order parameters at the temperatures -10 to 80 °C. |S| has been calculated according to Equation 3, using χ=172 kHz. θ_0 is the cone angle for the SHBS headgroup reorientation calculated according to Equation 4.

T(°C)	Δ(90) (kHz)	|S|	θ_0(deg)
-10	12.0	0.744	35.1
0	11.8	0.732	36.0
10	11.4	0.707	37.8
25	10.8	0.670	40.5
40	10.7	0.664	40.9
65	10.3	0.639	42.6
80	10.3	0.639	42.6

Figure Legends

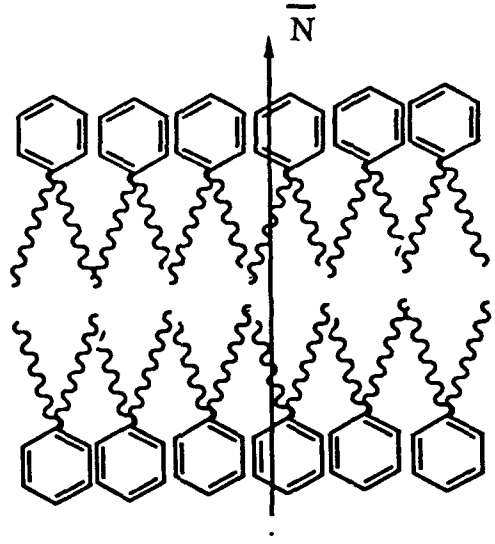
Figure 1. (A) Illustration of a lamellar liquid crystal or a bilayer adsorbed on a solid surface, with the normal to the bilayer (or director), **N**. (B) The geometrical relationships between the symmetric 1-4-axis, **M**; the director, **N**; and the external magnetic field, $\mathbf{B_0}$ (Only the phenyl ring is shown). The sulfonate group and the alkyl chain are attached along **M**. The angle between these are denoted α, β, and γ as shown. The sulfonate groups have been omitted in both cases.

Figure 2. The ^{2}H NMR spectra of SHBS-d_4 at 25 °C (A) adsorbed on γ-alumina at low surface coverage, sample I; (B) adsorbed at high coverage, sample II; (C) in a 2 % (w/w) water solution; and (D) in liquid crystals with water.

Figure 3. The ^{2}H NMR spectra of SHBS-d_4 adsorbed on γ-alumina at the adsorption plateau, from -30 °C to 80 °C. The tops of the 65 °C and 80 °C spectra have been cut off to show the quadrupole pattern. An expanded spectrum at 25 °C is also shown to most clearly show the features of the powder pattern.

Figure 4. The ^{2}H NMR spectra of SHBS-d_4 adsorbed on γ-alumina at low coverage, from -20 °C to 65 °C.

A



B

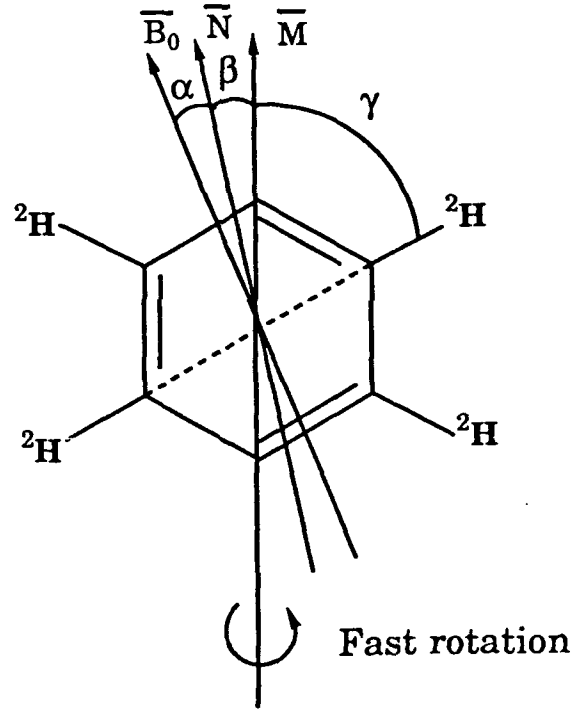


Figure 1

Fig 2

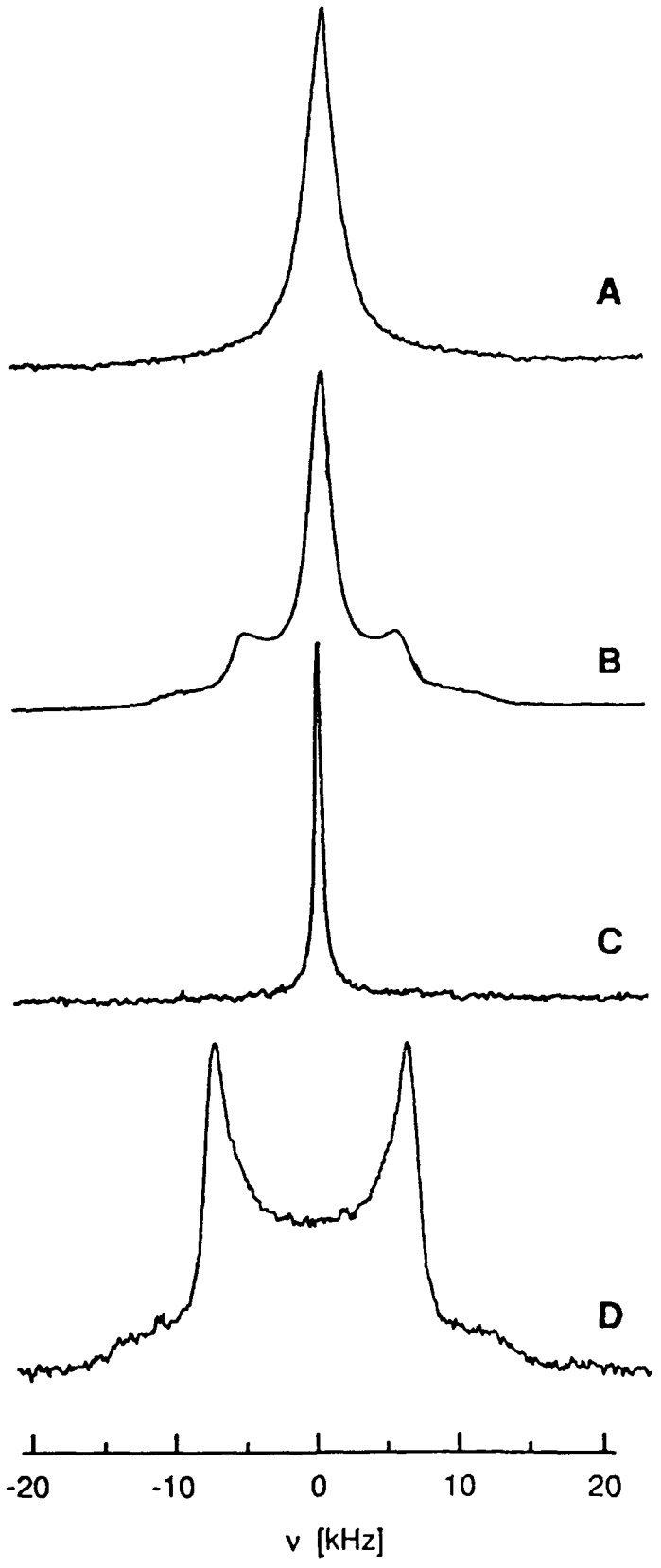


Fig 3

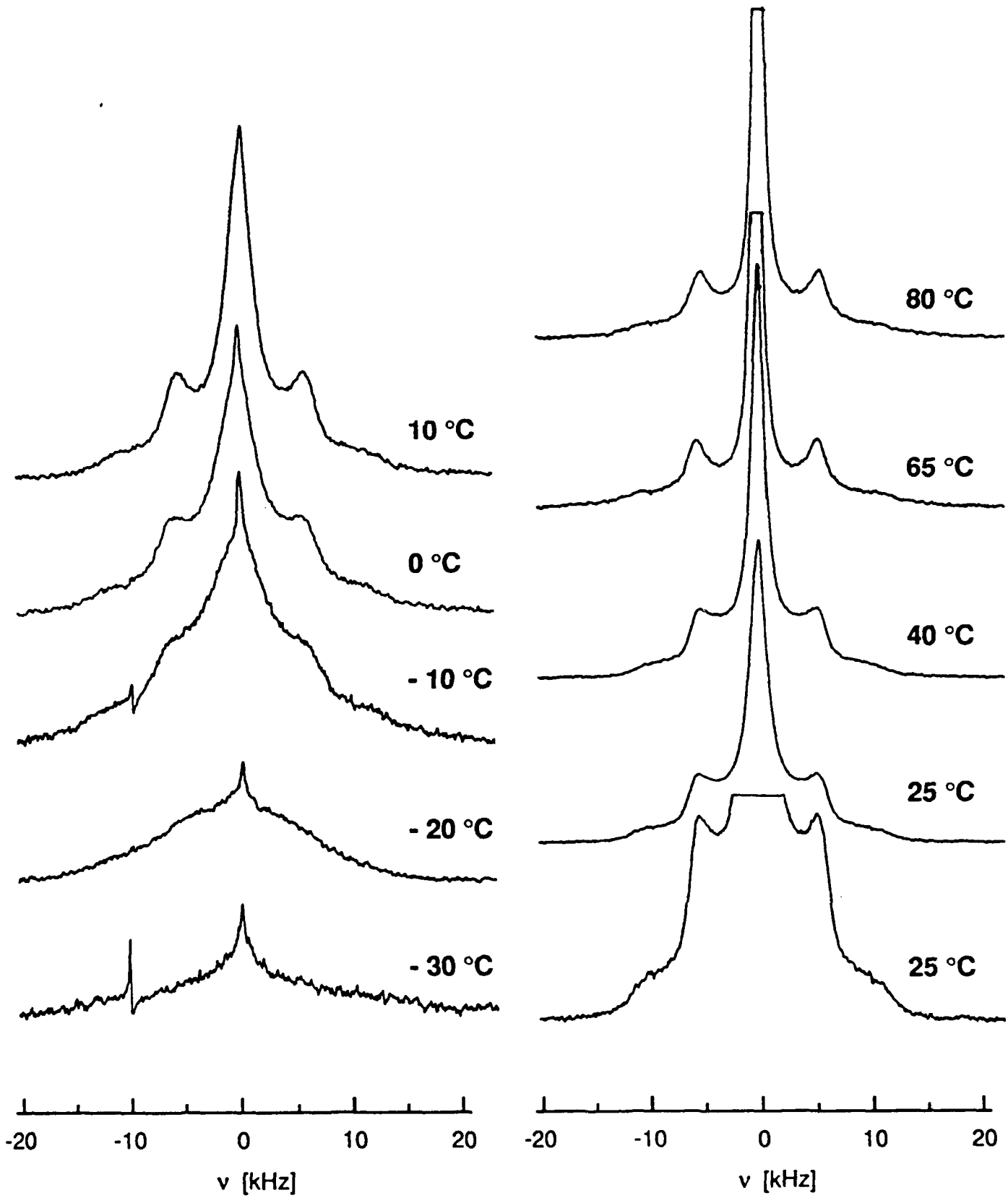

10 °C
0 °C
- 10 °C
- 20 °C
- 30 °C
80 °C
65 °C
40 °C
25 °C
25 °C
-20
-10
0
10
20
ν [kHz]
-20
-10
0
10
20
ν [kHz]

Fig 4